

FIRE RESISTANT MATERIAL

The present invention relates to inorganic-organic hybrids (IOHs), methods for their preparation and their use as fire resistant materials or components of fire resistant materials. More specifically, the invention relates to polyamide fire resistant formulations containing IOHs which have application in the production of fire resistant articles or parts thereof for use in the transportation, building, construction and electrical or optical industries.

BACKGROUND OF THE INVENTION

Materials based on organic polymeric systems (plastics) are widely used in the transportation, building and construction industries. A drawback of many types of organic polymers is flammability which limits their suitability in applications requiring flammability resistance and where regulatory authorities govern flammability standards.

In commercially produced polymeric systems, flame-retarding species may be added during processing or forming of the materials to reduce the end products flammability. Conventional flame-retardants may be divided into different categories including:

Halogen based: which consist of either brominated or chlorinated chemicals such as brominated polystyrene or phenylene oxide (Dead Sea Bromine or Great Lakes CC) or bis(hexachlorocyclopentadieno) cyclooctane (Occidental CC).

Phosphorus based: which consist of a range of different chemistries from elemental phosphorus (Clarient), phosphonates (A&W antiblaze 1045), phosphonate esters (Akzo Nobel), phosphites, phosphates and polyphosphates including melamine phosphite and phosphate, ammonium and melamine polyphosphate (DSM Melapur).

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Nitrogen based: such as melamine and its salts (US 4,511,684 Schmidt & Hoppe).

Intumescent agents: incorporating (i) an acid source (carbonization catalyst) such as ammonium polyphosphate; (ii) a carbonization reagent e.g. polyhydric alcohols such as pentaerythritol; and (iii) a blowing reagent like melamine. Expandable graphite is also known to undergo thermal expansion on addition of heat.

Inorganic additives: such as magnesium hydroxide and aluminum hydroxide (Martinswerk), zinc borate (Fire Brake ZB, US Borax) and antimony trioxide.

Although the addition of fire retardants to polymeric systems may improve their fire performance other important properties are often adversely effected for example:

- Mechanical performance
- Surface finish
- Durability
- Rheology
- Stability
- Smoke generation
- Toxicity
- Cost
- Recyclability

Furthermore, there has been considerable recent impetus to reduce the use of some flame-retardant classes due to toxicological or environmental concerns. Such legislation has placed pressure on the use of halogenated compounds and certain metal oxide synergists. Phosphorus-based flame-retardants such as phosphonates and elemental (red) phosphorus are also undesirable due to their regulation under chemical weapon acts and considerable manufacturing danger.

As far back as 1965, Jonas (GB_1114,174) teaches that the incorporation of organically modified clay into plastics reduces melt dripping during combustion.

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More recently it has been shown that under certain synthetic or processing conditions, organically modified clay may be nano-dispersed into polymeric materials to improve mechanical and fire performance.

5 Okada et al, (US 4,739,007 (1988) Toyota) teaches that nylon 6 materials with improved mechanical and heat distortion temperature can be prepared by adding suitably modified clay during the synthesis of nylon 6. In this case the growing nylon chains force apart the clay
10 platelets to form intercalated or exfoliated nanomaterial structures (so called in 'situ polymerisation' method).

A more commercially desirable method of nano-dispersing modified clay is described by Maxfield, et al, (WO 93/04118 WO 93/04117 (1993) Allied Signal). Maxfield
15 teaches that clay-plastic nanomaterials with improved mechanical and heat distortion performance may be prepared by subjecting functionalised clay and molten plastics such as nylon6, nylon66 and PBT to shear forces.

Others have investigated the fire performance of
20 plastics incorporating clay nano particles. Gilman has studied the fire performance of nylon-nanomaterials prepared through the 'in situ' polymerisation pathway using cone calorimetry (Proc. 43. Int. SAMPE Sympos., (1998), p1053-1066, Fire and Materials, 24, (2000), p201-
25 208, Applied Clay Science, 15, (1999), p31-49). Improved heat release rates were achieved with the addition of commercially modified clay, without increasing toxic gas or smoke generation. Gilman teaches that the improved fire performance results from the nanoparticles both
30 mechanically stabilizing the char and enhancing its barrier properties. Although Gilman's cone calorimetry tests suggest improved performance in terms of a reduction in heat release rate, no mention was made of other aspects of the materials fire performance in common tests
35 described by bodies such as ASTM and FAA which are used to assess, regulate and qualify the fire worthiness of materials.

Other groups have reported that traditional flame-retardants and nano-dispersed clays can act synergistically to improve fire performance.

5 Klatt (WO 98/36022, (1998) BASF) teaches that nylon materials incorporating organically modified clay and red phosphorus synergistically improve fire performance to produce a VO rating in UL94 type vertical burn tests. However, such compositions are undesirable due to the danger associated with handling of elemental
10 phosphorus.

Morton (WO 99/43747, (1999) General Electric Company) teaches that in certain polyester blends, phosphorus based flame retardants especially resorcinol diphosphate and organically modified clay act
15 synergistically to improve fire performance. No mention, however, is made of other important aspect such as the effect on mechanical performance, smoke and toxic gas emission.

Takekoshim (US 5,773,502 (1998) General Electric Company) teaches that conventional halogenated-Sb₂O₃ flame-retardant systems and organically modified clay can act synergistically. Takekoshim claims that nano-dispersed clay allows for reductions in the amount of Sb₂O₃ and halogenated flame retardant required to maintain a VO
20 rating in the UL 94 flammability test. Clearly any use of halogenated flame retardant is undesirable.

Masaru, T (JP 10182141 (1998) Sumitoma, Chem Co.) disclose a fire resistant and thermally expandable material at temperatures between 100 to 150°C whereby
30 blowing reagents such as those containing azo, diazo, azide or triazine compound are located between the layers of the silicate. In many polymeric systems, however, this flame retarding system is undesirable since they require moulding or forming at temperatures between 100°C to 150°C.

35 Inoue and Hosokawa (JP 10081510 (1998) Showa Denko K.K.) investigated the use of fluorinated synthetic mica exchanged with melamine (0.1 - 40%) and melamine

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salts (<10%) as a means of flame proofing plastics in a two step extrusion process. They claim that a VO rated Nylon6 (UL94 vertical burn test) was achieved at a loading of 5 percent-modified mica when greater than 80%
5 exfoliation occurred. The use of synthetic clays and multiple step processing is clearly undesirable from a commercial viewpoint. Inoue and Hosokawa do not disclose highly desirable chemistries and methodologies associated with triazine based formulations which effect mechanical
10 and fire performance. Furthermore, they do not disclose important methodologies to flame retarded thin parts known by those in the art to be extremely difficult to render flame resistant whilst simultaneously reducing toxic gas and smoke generation during combustion.

15 In a later disclosure Inoue, H., and co-workers (US 6294599 (2001) Showa Denko K.K.) also teach that polyamides reinforced with fibrous additives may be rendered flame resistant through the addition of triazine-modified clay and additional flame retardant. They
20 describe a highly rigid flame-retardant polyamide comprising a polyamide, silicate - triazine compound reinforcement and flame retardant/adjunct. The poor rheological properties of highly rigid polyamide formulations limit the inventions usefulness in preparing
25 components made by conventional processing techniques such as rotational or blow moulding, that are complex or thin walled or which require high ductility or impact performance.

Brown, S.C. et al (WO 00/66657, Alcan
30 International) disclose a polymeric material incorporating Cloisite montmorillonite in combination with $\text{Al}(\text{OH})_3$ for the production of fire resistant cables. This strategy is clearly only suitable for plastics that are processed at low temperatures considering that $\text{Al}(\text{OH})_3$ decomposes to
35 release water vapor at temperatures above approximately 190°C .

Accordingly, there is a need for the development of new flame retarding systems which both meet the performance criteria associated with specific applications and address the above concerns.

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SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided an inorganic-organic hybrid (IOH) which comprises:

- 10 (i) an expandable or swellable layered inorganic component; and
- (ii) an organic component including at least one ionic organic component.

15 Preferably, the organic component of the IOH also includes one or more neutral organic components which are intercalated between and/or associated with the layer(s) of the inorganic component.

20 According to another aspect of the present invention there is provided a method for the preparation of the IOH defined above which comprises mixing components (i) and (ii) defined above or constituents thereof in one or more steps.

 The present invention also provides the use of the IOH defined above as a fire resistant material.

25 According to a further aspect of the present invention there is provided a fire resistant formulation which comprises:

- (i) the IOH defined above; and
- (ii) one or more flame retardants.

30 According to a still further aspect of the present invention there is provided a method for the preparation of the fire resistant formulation defined above which comprises mixing components (i) and (ii) as defined above or constituents thereof in one or more

35 steps.

 The present invention also provides a polyamide fire resistant formulation which comprises either:

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- (A) (i) the IOH defined above; and
(ii) a polyamide based matrix; or
(B) (i) the fire resistant formulation defined
above; and
5 (ii) a polyamide based matrix.

The present invention further provides a method
for the preparation of the polyamide fire resistant
formulation defined above which comprises dispersing the
IOH or the fire resistant formulation defined above or
10 constituents thereof into the polyamide based matrix in
one or more steps.

The IOH and/or fire resistant formulations of
the present invention may be used to produce fire
resistant articles or parts thereof.

15 Thus, the present invention provides a fire
resistant article or parts thereof which is composed
wholly or partly of the IOH and/or fire resistant
formulations defined above.

The present invention also provides a method of
20 preparing the fire resistant article or parts thereof
defined above which comprises moulding or forming the IOH
and/or fire resistant formulations defined above.

DETAILED DESCRIPTION OF THE INVENTION

25 For the purposes of this specification it will
be clearly understood that the word "comprising" means
"including but not limited to", and that the word
"comprises" has a corresponding meaning. It should also be
noted that for the purposes of this specification the
30 terms "swellable" and "expandable" relating to the layered
inorganic component are interchangeable.

The inorganic component is a
swellable/expandable layered inorganic based material,
rendered positively (or negatively) charged due to
35 isomorphic substitution of elements within the layers,
such as, those based on a 1:1 layered silicate structure
such as kaolin and serpentine and a 2:1 layered silicate

structure such as phyllosilicates, talc and pyrophyllite. Other useful layered minerals include layered double hydroxides of the general formula $\text{Mg}_6\text{Al}_{3.4}(\text{OH})_{18.8}(\text{CO}_3)_{1.7}\cdot\text{H}_2\text{O}$ including hydrotalcites and synthetically prepared layered materials including synthetic hectorite, montmorillonite, fluorinated synthetic mica and synthetic hydrotalcite.

The group consisting of naturally occurring or synthetic analogues of phyllosilicates is particularly preferred. This group includes smectite clays such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, bentonite, saponite, sauconite, magadiite, kenyaite, laponite, vermiculite, synthetic micromica (Somasif) and synthetic hectorite (Lucentite). Other useful layered minerals include illite minerals such as ledikite and mixtures of illite minerals with said clay minerals.

Naturally occurring phyllosilicates such as bentonite, montmorillonite, and hectorite are most preferred. Such phyllosilicates with platelet thicknesses less than about 5 nanometers and aspect ratios greater than about 10:1, more preferably greater than about 50:1 and most preferably greater than about 100:1 are particularly useful.

The preferred inorganic materials generally include interlayer or exchangeable metal cations to balance the charge, such as, alkali metals or alkali earth metals, for example, Na^+ , K^+ , Mg^{2+} or Ca^{2+} , preferably Na^+ . The cation exchange capacity of the inorganic material should preferably be less than about 400 milli-equivalents per 100 grams, most preferably about 50 to about 200 milli-equivalents per 100 grams.

The organic component includes one or more ionic species that may be exchanged with the exchangeable metal ions associated with the inorganic component and optionally one or more neutral organic species which are intercalated between and/or associated with the layer(s)

of the inorganic component and/or one or more coupling reagents.

The term "associated with" is used herein in its broadest sense and refers to the neutral organic component being attached to the layer(s) of the inorganic component, for example, by secondary bonding interactions, such as, Van der Waals interactions or hydrogen bonding or trapped by steric limitation.

Suitable examples of ionic species include those that contain onium ions such as ammonium (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or aryl-aliphatic amines, phosphines and sulfides.

Such compounds may be prepared by any method known to those skilled in the art. For example, salts prepared by acid-base type reactions with mineral or organic acids including hydrochloric, sulfuric, nitric, phosphoric, acetic and formic acids, by Lewis-acid - Lewis-base type reactions or by reaction with alkyl halides to form quaternary salts for example using Menschutkin type methodology.

Ionic or neutral compounds which are known to decompose or sublime endothermically, and/or which release volatiles with low combustibility on decomposition and/or induce charring of organic species during thermal decomposition or combustion are particularly preferred.

Suitable species include neutral or ionic derivatives of nitrogen based molecules, such as, triazine based species, for example, melamine, triphenyl melamine, melam (1,3,5-triazine-2,4,6-triamine-n-(4,6-diamino-1,3,5-triazine-yl)), melem ((-2,5,8-triamino-1,3,4,6,7,9,9b-heptaazaphenalene)), melon (poly{8-amino-1,3,4,6,7,9,9b-heptaazaphenalene-2,5-diyl}imino)), bis and triaziridinyltriazine, trimethylsilyltriazine, melamine cyanurate, melamine phthalate, melamine phosphate, melamine phosphite, melamine phthalimide, dimelamine phosphate, phosphazines and/or low molecular weight

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polymers with triazine and phosphazine repeat units or salts or derivatives of the above molecules including onium ion derivatives or salts or derivatives of isocyanuric acid, such as, isocyanuric acid, cyanuric acid, triethyl cyanurate, melamine cyanurate, triglycidylcyanurate, triallyl isocyanurate, trichloroisocyanuric acid, 1,3,5-tris(2-hydroxyethyl)triazine-2,4,6-trione, hexamethylenetetramine. melam cyanurate, melem cyanurate and melon cyanurate.

Reagents known to induce charring of organic species include derivatives of phosphoric acid or boric acid, such as ammonia polyphosphate and melamine polyphosphate, melamine phosphate ammonium borate.

In another embodiment of the invention, the preferred ionic compounds may be optionally used in combination with other ionic compounds, for example, those known to improve compatibility and dispersion between the layered inorganic material and polymeric matrices such as those described in WO 93/04118 for the preparation of nanomaterials. Amphiphilic molecules that incorporate a hydrophilic ionic group along with hydrophobic alkyl or aromatic moieties are preferred.

One or more coupling reagents may also be associated with the inorganic component. Suitable coupling reagents include organically functionalised silanes, zirconates and titanates. Examples of silane coupling reagents include tri-alkoxy, acetoxy and halosilanes functionalised with amino, epoxy, isocyanate, hydroxyl, thiol, mercapto and/or methacryl reactive moieties or modified to incorporate functional groups based on triazine derivatives, long chain alkyl, aromatic or alkylaromatic moieties. Examples of zirconate and titanate coupling reagents include Teaz and Titan1.

It is known in the art that metal cations or anions associated with layered inorganic materials may be exchanged with organic ions through ion exchange

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processes. In a typical process, the layered inorganic material is first swollen or expanded in a suitable solvent(s) prior to ion exchange and then collected from the swelling solvent following agglomeration using methods
5 such as filtration, centrifugation, evaporation or sublimation of the solvent. Ion exchange techniques with suitable molecules are known to be a useful method of increasing the compatibility between clay and organic polymeric binders, thus aiding dispersion of clay
10 platelets into polymeric based matrices on a nanometer scale.

We have discovered that the ion exchange process may be optionally carried out in the presence of one or more types of organic ion to produce an inorganic-organic
15 hybrid with a plurality of functions. Without wishing to limit the present invention, such functions may include the presence of ions which promote dispersion, compatibility and interactions with the plastic matrix and ions useful to improve other properties such as fire
20 performance. Generally during ion exchange the organic ions are added in molar excess of the ion exchange capacity of the inorganic material, preferably less than about 10-fold excess, more preferably less than about a 5-fold excess is required.

It has also been unexpectedly discovered that the ion exchange processes may be carried out in the presence of functional dissolved or partially dissolved neutral species. Without being limited by theory, it is proposed that at least a portion of the neutral species
30 are trapped in the intergallery region or otherwise associated with the layered inorganic material following ion exchange. Such a process provides a useful mechanism of dispersing neutral additives on a molecular level into plastics. Again without being limited by theory, during
35 melt processing at least partial exfoliation of the inorganic-organic hybrid allows the neutral molecules to diffuse away and become homogeneously dispersed with the

matrix on a molecular level. This has a major impact on the performance of the resultant material since it is well known that efficient dispersion of all components in a plastic formulation, preferably on a nano- or molecular scale, is an important factor for achieving optimum performance.

In another aspect of the invention, the IOH may be treated prior, during or following ion exchange with one or more coupling reagents as described above. The coupling reagents are derivatized to improve, for example, the compatibility and interactions between the inorganic phase and polymeric matrix or to attach other desirable functionalities to the inorganic layered phase.

Suitable flame retardants which retard flame propagation, heat release and/or smoke generation which may be added singularly or optionally synergistically to the IOH include:

- Phosphorus derivatives such as molecules containing phosphate, polyphosphate, phosphites, phosphazine and phosphine functional groups, for example, melamine phosphate, dimelamine phosphate, melamine polyphosphate, ammonia phosphate, ammonia polyphosphate, pentaerythritol phosphate, melamine phosphite and triphenyl phosphine.
- Nitrogen containing derivatives such as melamine, melamine cyanurate, melamine phthalate, melamine phthalimide, melam, melem, melon, melam cyanurate, melem cyanurate, melon cyanurate, hexamethylene tetraamine, imidazole, adenine, guanine, cytosine and thymine.
- Molecules containing borate functional groups such as ammonia borate and zinc borate.
- Molecules containing two or more alcohol groups such as pentaerythritol, polyethylene alcohol, polyglycols and carbohydrates, for example, glucose, sucrose and starch.
- Molecules which endothermically release non-combustible decomposition gases, such as, metal

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hydroxides, for example, magnesium hydroxide and aluminum hydroxide.

- Expandable graphite

The polyamide based matrix may be included in the fire resistant formulation in pellet, granule, flake or powdered form. Suitable polyamides comprise generic groups with repeat units based on amides, such as, Nylon4, Nylon6, Nylon7, Nylon 11 and Nylon12, Nylon46, Nylon66, Nylon 68, Nylon610, Nylon612 and aromatic polyamides, for example, poly'm'phenyleneisophthalamine and poly'p'phenylene'terephthalamide.

It will be appreciated that the polyamide based matrix may include co-polymers, blends and alloys. The co-polymers may be made up of two or more different repeat units one of which is an amide. Such co-polymers may be prepared by any suitable methods known in the art, for example, at the point of initial polymerisation or later through grafting or chain extension type reactions during processing. The polyamide blends and alloys may be prepared using any method known to those skilled in the art including melt or solution blending. Blending or alloying the polyamide with other polymers may be desirable to improve properties such as toughness, modulus, strength, creep, durability, thermal resistance, conductivity or fire performance.

Nylon12, Nylon6 and Nylon66 and their respective co-polymers, alloys and blends are particularly preferred.

The polyamide formulation can also optionally contain one or more additives known in the art of polymer processing, such as, polymeric stabilisers, for example, UV, light and thermal stabilisers; lubricants; antioxidants; pigments, dyes or other additives to alter the materials optical properties or colour; conductive fillers or fibers; release agents; slip agents; plasticisers; antibacterial or fungal agents, and processing agents, for example, dispersing reagents, foaming or blowing agents, surfactants, waxes, coupling

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reagents, rheology modifiers, film forming reagents and free radical generating reagents.

A particularly preferred formulation comprises Nylon12, Nylon6 and/or Nylon66; montmorillonite modified with melamine hydrochloride and/or melamine; melamine cyanurate and/or melam (1,3,5-triazine-2,4,6-triamine-n-(4,6-diamino-1,3,5-triazine-yl)) cyanurate, and/or melem ((-2,5,8-triamino-1,3,4,6,7,9,9b-heptaazaphenalene)) cyanurate and/or melon (poly{8-amino-1,3,4,6,7,9,9b-heptaazaphenalene-2,5-diyl}imino)) cyanurate; magnesium hydroxide; and one or more additives.

The polyamide formulation preferably contains a polyamide based matrix in an amount of from about 50 to about 95% w/w, an IOH in an amount less than about 25% w/w and optionally a flame retardant and/or additives in an amount less than about 30% w/w, but in some cases preferably above about 10% w/w.

It has been discovered that the IOH may be readily dispersed into the polyamide based matrix during the compounding (mixing) stage. Without wishing to be limited by theory, it is proposed that ion exchange enhances the layered IOHs compatibility with polyamides compared with unmodified inorganic layered materials. This heightened compatibility in combination with sufficient mixing forces, appropriate mixing sequence, screw design and time allows the organically modified platelets associated with the IOH to be at least partially exfoliated into the polyamide and hence dispersed at least partially on a nanometer scale. This process also provides a useful mechanism of dispersing into the polyamide any neutral molecules associated with the IOH on a molecular level.

Dispersion of the various components of the fire resistant formulation including the IOH is aided by grinding prior to mixing. Grinding is achieved using any suitable grinding equipment including ball mills, ring mills and the like. It is preferable that the components

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including the IOH is ground to a particle size less than about 200 microns, more preferably less than about 50 microns, most preferably less than about 20 microns. The hybrid material may also be ground using specialty grinding equipment allowing grinding to nanometer sizes.

Dispersion may be affected using any suitable melt, solution or powder based mixing process allowing sufficient shear rate, shear stress and residence time to disperse the IOH at least partially on a nanometer scale. Such processes may be conducted using milling procedures such as ball milling, in a batch mixer using internal mixers, such as, Banbury and Brabender/Haake type mixers, kneaders, such as, BUS kneaders, continuous mixing processes including continuous compounders, high intensity single and twin screw extrusion.

Melt processing is preferred and in a particularly preferred embodiment, twin screw extruders with an L:D ratio of at least about 24, preferably more than about 30 equipped with at least one and preferably multiple mixing and venting zones are employed for dispersion. Such screw configurations useful for dispersive and distributive mixing are well known to those in the art. A particularly useful system has been found to be that illustrated in Figure 1.

The components of the formulation may be added in any order or at any point along the extruder barrel. Since polyamides are susceptible to hydrolysis it is preferable that the components are dried prior to processing and/or mechanisms to remove water vapor such as vents or vacuum ports available during processing. In a preferred embodiment, all of the components are added at one end of the extruder. In another preferred embodiment, a polymeric binder and optionally minor components are added at one end of the extruder and the IOH and optionally minor components at a later point/s. In still another preferred embodiment, the IOH portion of the polymeric binder and optionally minor components are added

at one end of the extruder with the remaining portion of the polymeric binder and optionally minor components are added at a later point/s. Following extrusion the molten composition is cooled by means of water bath, air knife or atmospheric cooling and optionally cut into pellets.

Preferably all of the major and minor components of the system can be combined in as few a mixing steps as possible, most preferably in a single mixing step.

The moulding or forming of the polyamide formulation into fire resistant articles or parts thereof can be carried out using any method known to those in the art including processes such as extrusion, injection moulding, compression moulding, rotational moulding, blow moulding, sintering, thermoforming, calending or combinations thereof.

In one embodiment of the invention the fire resistant polyamide system containing the major and minor components is moulded or formed into parts having wall thickness less than about 25 mm, preferably less than about 5 mm, most preferably less than 1.5 mm. Such parts include but are not limited to tubes, complex moulded hollow parts, sheets and complex moulded sheets and other complex objects that are moulded or formed using techniques, such as, extrusion, injection moulding thermoforming and rotational moulding.

In the simplest process, the article or part is directly produced during compounding for example by locating a die at the end of the extruder allowing the shape of the extrudate to be modified as required. Examples of such components include simple parts such as film, tape, sheet, tube, rod or string shapes. The process may also involve multiple layers of different materials one of which being the said polymeric system built up by processes known to those in the art including co-extrusion.

In another preferred embodiment, the formulation is moulded or formed in a separate step using techniques

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such as injection, compression or blow moulding. Such parts are generally more complex in nature compared with parts formed by extrusion alone, their design only limited by the requirements of the moulding tool / process employed. Suitable examples include but are not limited to stowage bin hinge covers, ECS duct spuds, latches, brackets, passenger surface units and the like.

It is noted that for certain applications it may be preferable that the fire resistant polyamide formulation is ground to a powder. In such cases it has unexpectedly been found that grinding of the said formulation using cryogenic or atmospheric grinding techniques known to those in the art may be carried out without significantly effecting the performance of the system. Such moulding applications include selective laser sintering, rotational moulding, and extrusion. Suitable examples including but not limited to environmental control systems (air-conditioning ducts) and the like.

In other preferred applications, the polymeric formulation may be first formed into a sheet or film, for example, through extrusion, blow moulding, compression moulding or calendering. The sheet may be subsequently moulded to a desired shape using thermoforming techniques. In yet another application, the sheet or film may be used to prepare reinforced thermoplastic laminates with woven fabrics prepared from surface modified or natural glass, carbon or aramid using techniques such as compression moulding or resin infusion/transfer. Again, the laminate sheet hence formed may be further moulded to a desired shape using techniques such as thermoforming.

Alternatively the formulation may be spun into fibres by any method known to those skilled in the art. Such a process provides a method for producing fire resistant fabrics, carpets and alike

The present invention is useful for producing polyamide materials with favourable rheological properties

for moulding including thin or intricate articles or parts thereof which maintain mechanical properties close to or exceeding that of the virgin polyamide matrix and which show improved fire performance in standard tests through
5 resisting combustion by self-extinguishing when ignited, limiting flame propagation, and generating low smoke and toxic gas emissions. Such articles or parts thereof are useful for applications which require superior fire
10 performance and in industries that are regulated for fire performance including transport, for example, air, automotive, aerospace and nautical; building and construction; and electrical or optical, for example, cables, wires and fibres.

15 BRIEF DESCRIPTION OF THE DRAWINGS

In the examples, reference will be made to the accompanying drawings in which:

Figure 1 is a diagram showing the twin screw extruder screw and barrel configuration;

20 Figure 2 is a graph showing the XRD results and transmission electron microscope (TEM) image for Example 7;

Figure 3 is a graph showing the XRD results for Example 8;

25 Figure 4 is a graph showing the XRD results for Example 9;

Figure 5 is a graph showing XRD results for Example 17; and

30 Figure 6 is a picture of complex hollow fire resistant components moulded with formulations 13 and 34.

EXAMPLES

The invention will now be described with reference to the following non-limiting examples.

35

General Conditions & Reagents

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Tables 1, 2 and 3 Outline General Reagents,
Conditions & Procedures associated with the examples.

Table 1: Commercially Available Reagents

Reagent	Trade name	Supplier
Montmorillonite – organic modified	Cloisite 93A	Southern Clay
Montmorillonite – organic modified	Cloisite 30B	Southern Clay
Montmorillonite	Cloisite Na ⁺	Southern Clay
Synthetic Hectorite	Laponite	Southern Clay
Nylon12	Vestamid 9005	Degussa
Nylon12 FR (Flame retarded)	Vestamid 7166	Degussa
Polyetherimide	Ultem 9075	GE Plastics
Nylon6	Akulon PA6	DSM
Nylon66	Akulon PA66	DSM
Cyanuric acid	Cyanuric acid	Aldrich
Melamine cyanurate	Fyrol MC	Akzo-Nobel
Melamine phosphate	Fyrol MP	Akzo-Nobel
Melamine polyphosphate	Melapur 200	DSM Melapur
Melamine	Melamine	Aldrich
Pentaerythritol	Pentaerythritol	Aldrich
Magnesium hydroxide	Magnifin	Martinswerk
Ammonia polyphosphate	Antiblaze MC	Rhodia
Pentaerythritol phosphate	NH-1197	Great Lakes
Pentaerythritol phosphate Blend	NH-1511	Great Lakes
Zinc borate	Fire Brake ZB	US Borax
Zn Stearate	Zincum	Baerlocher
Ca Stearate	Ceasit	Baerlocher
Int 38	Synthetic resin	AXEL
LuWax Eas1	Ethylene co-polymer	BASF
Irganox b1171	Phosphite/hindered phenol blend	CIBA

Table 2: Processing Equipment and Conditions

Equipment	Type																																										
Twin screw extruder	<p>Berstorff ZE 25 mm modular co-rotating twin screw extruder coupled to a Haake Rheocord motor drive and torque cell for rheology measurement</p> <p>L:D ratio = 36:1</p> <p>Screw and barrel configuration presented in Figure 1,</p> <p>Screw speed 300 rpm</p> <p>Feed rate ~1.2 Kg/hour</p> <p>Residence time average 2 min</p> <p>Flat 200°C temperature profile from throat to die (nylon12)</p> <p>Flat 250°C temperature profile from throat to die (nylon6)</p> <p>Flat 275°C temperature profile from throat to die (nylon66)</p>																																										
Batch Mixer	<p>Haake R3000 batch mixer connected to torque rheological load cell, pneumatic ram, roller rotors</p> <p>Rotor speed – 5 min 60 rpm, 10 min 120 rpm</p> <p>Temperature 190°C</p>																																										
Injection Moulding	<p>Battenfeld 80 ton BA 800 CDC injection moulding machine</p> <p>Temperature profile:</p> <table><tr><td>Nylon12</td><td>Zone</td><td>1</td><td>2</td><td>3</td><td>Nozzle</td><td>Die</td></tr><tr><td>Temp (°C)</td><td></td><td>215</td><td>220</td><td>225</td><td>225</td><td>70°C</td></tr></table> <table><tr><td>Nylon6</td><td>Zone</td><td>1</td><td>2</td><td>3</td><td>Nozzle</td><td>Die</td></tr><tr><td>Temp (°C)</td><td></td><td>230</td><td>230</td><td>250</td><td>260</td><td>90°C</td></tr></table> <table><tr><td>Nylon 66</td><td>Zone</td><td>1</td><td>2</td><td>3</td><td>Nozzle</td><td>Die</td></tr><tr><td>Temp (°C)</td><td></td><td>260</td><td>260</td><td>280</td><td>290</td><td>90°C</td></tr></table> <p>ASTM test samples:</p> <p>Injection pressure gradient 800 to 600 bar, cavity pressure 400 bar, Holding pressures 600 to 0 bar</p> <p>Cooling time 30sec</p> <p>Cone Calorimetry Samples:</p> <p>Injection pressure gradient 950 to 650 bar, cavity pressure 325 bar, Holding pressures 650 to 0 bar</p> <p>Cooling time 60 sec</p>	Nylon12	Zone	1	2	3	Nozzle	Die	Temp (°C)		215	220	225	225	70°C	Nylon6	Zone	1	2	3	Nozzle	Die	Temp (°C)		230	230	250	260	90°C	Nylon 66	Zone	1	2	3	Nozzle	Die	Temp (°C)		260	260	280	290	90°C
Nylon12	Zone	1	2	3	Nozzle	Die																																					
Temp (°C)		215	220	225	225	70°C																																					
Nylon6	Zone	1	2	3	Nozzle	Die																																					
Temp (°C)		230	230	250	260	90°C																																					
Nylon 66	Zone	1	2	3	Nozzle	Die																																					
Temp (°C)		260	260	280	290	90°C																																					

Table 2 cont

Equipment	Type
Compression Moulding	Assett 2.5 MPa pneumatic press, 45 cm platens, heating (400°C) and cooling Moulding platen temperature 220°C nylon12 Moulding platen temperature 260°C nylon6 Moulding platen temperature 290°C nylon66

Table 3: Characterization Techniques, Conditions and Sample Preparations

Equipment	Type
X-ray diffraction (XRD)	Phillips PW 1729, CuK α 1 source $\lambda = 0.154$ nm Powders were ground to a particle size of less than 100 micron, Plastics were compression moulded (210°C) to a thickness of 100 micron
Transmission Electron Microscopy (TEM)	Hitachi H-7500 operating at an electron potential of 120 kV 100 nm thick sections were prepared by ultra microtomy
Differential Scanning Calorimetry (DSC)	Cryogenic TA 2920 MDSC employing Advantage software, 10°C and 20°C/min ramp rate rates for heating and cooling for general thermal and glass transition respectively. Calibrated against, Indium, distilled water, cyclohexane and sapphire Powders were ground to a particle size of less than 100 micron. Plastics were compression moulded (210°C) to a thickness of 100 micron with quench cooling, 5mm diameter specimens were punched from the moulded sheet
Thermal Gravimetric Analysis (TGA)	Thermal Sciences, PL-STA, referenced against Al $_2$ O $_3$ Heating rate ramp 10°C / min Powders were ground to a particle size of less than 100 micron Plastics were compression moulded (210°C) to a thickness of 100 micron with quench cooling, 4mm diameter specimens were punched from the moulded sheet
Cone Calorimetry Testing	ASTM E 1354 - 92 Modified from the original Stanton-Redcroft model, employing CSIRO developed software Radiant flux 35 kW/m 2 , 3 repeats per sample, ASTM E1356 Following injection moulding, samples (100x100x6mm) were conditioned for 7 days at 23°C at 50% RH. Heat release, smoke, mass loss and gas emission were measured
Radiant Panel	Conducted as per FAA specification (DOT FAA/AR-0012) & as outlined in ASTM E648 - 93a

Table 3 cont.

Equipment	Type
Specific Optical Density of smoke Generated By combustion Solid Materials and gas emission	ASTM E662 – 93 for optical density with gas released by samples during the test analyzed for HF, HCl, HCN, H ₂ S, NO _x , HBr, PO ₄ , SO ₂
Vertical Burn	<p>Vertical burn tests according to UL94 or FAA specifications.</p> <p>UL94 specification –</p> <p>One 10 sec application of flame from a 10 mm burner to 125x12.3x3.2 mm samples according to UL specifications 2000. Flame extinguish times were monitored over at least 3 samples</p> <p>Extinguishing times, VO <10s, V1 <30s, V2 <30s</p> <p>Cotton Wool Ignition No No Yes</p> <p>FAA (DOT FAA/AR-0012) and ASTM F501-93</p> <p>12 s burn</p> <p>One 12s application of flame from a 10 mm burner to 300x75 mm samples according to FAA specification 2000: sample thickness specified</p> <p>Pass FAA test requirement:</p> <p>Flame extinguished <15sec</p> <p>Drip extinguished <5 sec</p> <p>Burn height <203 mm</p> <p>60 s burn</p> <p>One 60s application of flame from a 10 mm burner to 300x75 mm samples according to FAA specification 2000</p> <p>Pass FAA test requirement:</p> <p>Flame extinguished <15sec</p> <p>Drip extinguished <3 sec</p> <p>Burn height <150 mm</p> <p>Sample thickness specified</p>

Table 3 cont.

Equipment	Type
IZOD Notched Impact Testing	Radmana ITR 2000 instrumented impact tester Izod mode, Iact strain rate 3.5 ± 0.2 m/sec 10 repeats per sample, ASTM 256 Following injection moulding, samples were stored for 24 h in desiccated containers, notched according to the ASTM 256 standard and tested 'dry as moulded standard deviation generally less than 8%
Tensile Testing	Instron tensile testing apparatus (5565) utilizing a 30 kN load cell, 50 mm/min strain rate 5 repeats per sample as per ASTM D638 External extensometer used for independent modulus measurements ASTM D5938 Following injection moulding, samples were stored for 24 h in desiccated containers and tested 'dry as moulded Generally standard deviation less than 2% for modulus and strength results
MFI	MFI testing was completed according to ASTM D1238 standards employing 2.16 load at a temperature of 235°C, Employing a Davenport Melt Flow Indexer apparatus
Parallel Plate Rheology	The viscosities of samples were measured over a wide range of shear rate range of 10^{-2} to 10^1 s ⁻¹ at 240 °C. Tests of shear rate sweep were carried out using a shear strain-controlled rheometer, RDA II (Rheometric Scientific Inc.). The test fixture geometry used was 25 mm parallel-plate with a constant gap between 0.6 – 0.8 mm. The nitrogen gas was used to provide an inert testing environment to reduce sample degradation due to oxidation of samples.

**Methods for Preparing Inorganic-Organic hybrids (IOH) -
Examples 1-6**

5 **Example 1: Preparation of melamine hydrochloride
modified montmorillonite (IOH1)**

Montmorillonite exchanged Na⁺ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 80°C DI water (2% w/w) and mechanically stirred at 1500 rpm for 60 min.

10 Melamine monohydrochloride salt (1.4 mmol/100g montmorillonite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with

15 warm DI water and then preliminary dried (60 - 80°C). The resultant granular organically modified clay was ground to a particle size of less than 50 micron and then further dried at 75°C prior to processing or analysis.

20 **XRD** (CuK_{α1} source λ = 0.154 nm)

Cation	Na ⁺	Melamine.HCl modified Montmorillonite
XRD d₀₀₁	1.10 nm	1.27 nm

Results indicate that with ion exchange montmorillonite's intergallery spacing is increased from

25 *1.10 nm to 1.27 nm. This result is consistent with sodium ions being replaced by protonated melamine ions in the intergallery region during ion exchange.*

Example 2a: Preparation of melamine hydrochloride modified montmorillonite in the presence of melamine (IOH2)

- 5 Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 80°C DI water (2% w/w), melamine added (1.4 mmol/100 g montmorillonite) and the solution mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g
- 10 montmorillonite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm DI water and then preliminary dried (60 - 80°C). The
- 15 resultant granular organically modified clay was ground to a particle size of less than 50 micron and then further dried at 75°C prior to processing or analysis.

XRD ($\text{CuK}\alpha_1$ source $\lambda = 0.154 \text{ nm}$)

20

Cation	Na^+	Melamine and Melamine.HCl modified montmorillonite
XRD d_{001}	1.10 nm	1.39 nm

- Results indicate that montmorillonite modified by melamine hydrochloride in the presence of melamine has an expanded intergallery spacing compared with both*
- 25 *montmorillonite that is modified with melamine hydrochloride or sodium ions alone. The result is consistent association/entrapment of the neutral melamine with the clay during ion exchange.*

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Example 2b: Preparation of melamine hydrochloride modified montmorillonite in the presence of melamine (IOH2)

5 3.0Kg of sodium montmorillonite was dispersed into 200L de-ionized water at 60°C with vigorous stirring (200 rpm) adding the powder slowly over a period of approximately one hour to assist wetting out of the individual particles/platelets. After the suspension had stirred at
10 that temperature for approximately 2 hours, an aqueous solution (35L) containing 1.39 Kg melamine and 0.92L HCl (9.65M) at 85°C was rapidly added whilst the impeller speed was simultaneously increased to 300 rpm. After an initial period of high viscosity whilst the modified
15 montmorillonite aggregated, the viscosity decreased and the clay solution was allowed to stir for a further 3 hours at 60°C. Following filtration of the suspension the collected modified clay was re-dispersed into de-ionized water (150L) and allowed to stir for 1 hour at 60°C before
20 an aqueous solution (10 L) containing 0.385Kg melamine and 0.26 L HCl (9.65M) at approx 85°C was added. At this point the mixture was stirred for a further two hours before it was filtered. Next the modified clay was re-dispersed into de-ionized water (150L) and stirred for a further 1
25 hour at 60°C prior to filtration, drying and grinding of the modified clay to a particle size less than 50 micron.

XRD (CuK α 1 source λ = 0.154 nm)

Cation	Na ⁺	Melamine and Melamine.HCl modified Montmorillonite
XRD d₀₀₁	1.10 nm	1.40 nm

30

These results illustrate that the robustness of the modification procedure to variation in mole ratio of montmorillonite CEC to melamine salt and melamine and the reaction conditions employed to carry out the modification

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procedure. This result is consistent association/entrapment of the neutral melamine with the clay during ion exchange.

5 Example 2c: Preparation of melamine hydrochloride
 modified montmorillonite in the presence of
 melamine (IOH2)

15.0Kg of montmorillonite was dispersed into 200L de-
10 ionized water at 60°C with vigorous stirring (200 rpm)
 adding the powder slowly over a period of approximately 2
 hours to assist wetting out of the individual
 particles/platelets. After the suspension had stirred at
 that temperature for approximately 4 hours, an aqueous
15 solution (50L) containing 2.78Kg melamine and 1.84 L HCl
 (9.65 M) at 85°C was rapidly added whilst the impeller
 speed was simultaneously increased to 300 rpm. After an
 initial period of high viscosity whilst the modified
 montmorillonite aggregated, the viscosity decreased and
20 the clay solution was allowed to stir for a further 3
 hours at 60°C. Following filtration of the suspension the
 collected modified clay was re-dispersed into de-ionized
 water (150L) and allowed to stir for 1 hour at 60°C before
 an aqueous solution (25L) containing 1.925 Kg melamine and
25 1.3 L HCl (9.65M) at approx 85°C was added. At this point
 the mixture was stirred for a further two hours before it
 was filtered. Next the modified clay was re-dispersed
 into de-ionized water (200L) and stirred for a further 1
 hour at 60°C prior to filtration, drying and grinding of
30 the modified clay to a particle size less than 50 micron.

XRD (CuK α 1 source λ = 0.154 nm)

Cation	Na ⁺	Melamine and Melamine.HCl modified Montmorillonite
XRD d ₀₀₁	1.10 nm	1.40 nm

Results illustrate the robustness of the modification procedure to variation in reaction conditions employed to carry out the modification procedure. This result is consistent with association / entrapment of the neutral melamine molecules with the clay during ion exchange.

Example 3: Preparation of melamine cyanurate
 hydrochloride modified montmorillonite
 (IOH3)

Na⁺ exchanged montmorillonite (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 95°C distilled water (2% w/w), cyanuric acid added (1.4 mmol/100g montmorillonite) and the solution mechanically stirred at 1500 rpm for 60 min. Melamine mono-hydrochloride salt (1.4 mmol/100g montmorillonite) was then added to the solution and the resultant suspension with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried (75°C). The resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 60 - 80°C prior to processing or analysis.

XRD (CuK_{α1} source λ = 0.154 nm)

Cation	Na ⁺	Melamine cyanurate.HCl modified montmorillonite
XRD d₀₀₁	1.10 nm	1.42 nm

Results from Example 3 indicate that the intergallery spacing of montmorillonite is expanded further when exchanged with melamine cyanurate ion compared with sodium ion or melamine ion modified

montmorillonite alone (Example 1) due to its larger size and hence steric impact.

5 Example 4: Preparation of melamine and melamine
 cyanurate modified montmorillonite in
 presence of melamine and melamine cyanurate
 (IOH4)

10 Montmorillonite exchanged Na⁺ (Cation Exchange Capacity
 (CEC) = 92 meq/100g) was suspended in 95°C distilled water
 (2% w/w), cyanuric acid added (1.4 mmol/100 g
 montmorillonite) and the solution mechanically stirred at
 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4
15 mmol/100g montmorillonite) and melamine (1.4 mmol/100g
 montmorillonite) was then added to the solution and the
 resultant suspension continued stirring for a further 150
 min. Following filtration of the suspension, the
 precipitate was thoroughly washed with warm distilled
 water and then preliminary dried under vacuum (75°C). The
20 resultant granular organically modified clay was ground to
 a particle size of less than 45 micron and then further
 dried at 60 - 80°C prior to processing or analysis.

XRD (CuK_{α1} source λ = 0.154 nm)

25

Cation	Na ⁺	Melamine and Melamine cyanurate.HCl modified montmorillonite
XRD d₀₀₁	1.10 nm	1.53 nm

30 The results from Example 4 indicate that the
 intergallery spacing of montmorillonite exchanged with
 melamine cyanurate ion in the presence of melamine and
 melamine cyanurate is larger than both sodium ion or
 melamine cyanurate ion exchanged montmorillonite alone
 (Example 3). This result is consistent with

association/entrapment of the neutral melamine and melamine cyanurate with the clay during ion exchange.

5 Example 5: Preparation of melamine and trimethyl
cetylammonium and melamine hydrochloride
modified montmorillonite (IOH5)

Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 90°C distilled water (2% w/w), and the solution mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g montmorillonite) and trimethylcetylammmonium chloride (1.4 mmol/100g montmorillonite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried under vacuum (75°C). The resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 60 - 80°C prior to processing or analysis.

XRD (CuK α_1 source λ = 0.154 nm)

Cation	XRD d_{001}
Na ⁺	1.10 nm
Trimethylcetylammonium chloride	1.84 nm
Melamine and Trimethylcetylammonium chloride modified montmorillonite	1.68 nm

25

The results from Example 5 indicate that the intergallery spacing of montmorillonite exchanged with both trimethylcetylammonium chloride and melamine hydrochloride is larger than sodium but smaller than trimethylcetylammonium ion exchanged montmorillonite. This result is consistent with trimethylcetylammonium chloride

and melamine hydrochloride being present in the intergallery spacing of the modified montmorillonite.

5 Example 6: Preparation of melamine and melamine
 hydrochloride modified synthetic hectorite,
 laponite (IOH6)

10 Hectorite clay (Synthetic Laponite RD) was modified using
 the same general procedure as employed in Example 2 taking
 into consideration its lower cation exchange capacity
 (CEC) of 55 mmol/100g and employing a 1% solution for
 modification. Strict control was placed over the mole
 ratio of hectorite CEC and melamine salt to encourage
 platelet agglomeration. Following treatment with the
15 melamine salt/melamine, the modified synthetic clay was
 separated from the treatment solution by filtration.

XRD (CuK α 1 source λ = 0.154 nm)

Cation	Na ⁺ /Li ⁺	Melamine and Melamine.HCl Modified Hectorite
XRD d_{001}	1.20 nm	1.33 nm

20

 The results from Example 6 indicate that the intergallery spacing of synthetic hectorite exchanged with melamine hydrochloride in the presence of melamine is larger than sodium changed montmorillonite.

25

Melt Dispersion of Components and Formulation of Fire resistant Materials Examples 7-20

30 While each of the following examples use Nylon12, Nylon6 or Nylon66 as the polyamide based matrix, the person skilled in the art will appreciate that the examples for fire retarding nylon12, nylon6 and nylon66 are also applicable to other types of polyamides, polyamide co-polymers, polyamide blends, alloys and the like.

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The formulation constituents employed in Examples 7 to 20 are provided in Tables 4a to 4e.

Table 4a **Formulations used in Examples 7 to 20**

Formulation	Nylon12	Cloisite Na ⁺	Cloisite 30B	Cloisite 93A	IOH2 (Example2)	Melamine Cyanurate
1	99.25		0.75			
2	98.5		1.5			
3	95		5.0			
4	93		7.0			
5	95			5		
6	95	5				
7	82		3			15
8	83.5		1.5			15
9	84.25		0.75			15
10	85					15
11	82				3	15
12	83.5				1.5	15
13	84.25				0.75	15
14	84.5				3	12.5
15	86				1.5	12.5
16	86.75				0.75	12.5
17	87				3	10
18	88.5				1.5	10
19	89.25				0.75	10
20	90.5				3	7.5
21	91				1.5	7.5
22	91.75				0.75	7.5

Table 4b **Formulations used in Examples 7 to 20**

Formulation	Nylon12	IOH2 (Example 2)	Melamine Cyanurate	Magnesium Hydroxide (H7)	Melamine phosphate	Melamine poly phosphate	Melamine phthalate	Ammonia poly phosphate	Pentaerythritol phosphate	Pentaerythritol phosphate blend
23	83.5	1.5		15						
24	83.5	1.5			15					
25	83.5	1.5				15				
26	83.5	1.5					15			
27	83.5	1.5						15		
28	83.5	1.5							15	
29	83.5	1.5								15
30	83.5	1.5	10	5						
31	87.5		12.5							
32	98.5	1.5								

Table 4c
Formulations used in Examples 7 to 20

Formulation	Nylon12	IOH2 (Example 2)	Melamine cyanurate	Magnesium hydroxide (H7)	Magnesium hydroxide (H10)	Magnesium hydroxide (H5iv)	Magnesium hydroxide (H10iv)
33	82	3	12.5	2.5			
34	83.5	1.5	12.5	2.5			
35	84.25	0.75	12.5	2.5			
36	82	3	10	5			
37	84.25	0.75	10	5			
38	82	3	7.5	7.5			
39	83.5	1.5	7.5	7.5			
40	84.25	0.75	7.5	7.5			
41	83.5	1.5	12.5		2.5		
42	83.5	1.5	12.5			2.5	
43	83.5	1.5	12.5				2.5

Table 4d
Formulations used in Examples 7 to 20

Formulation	Nylon12	Nylon6	Nylon66	IOH1 (Example 1)	IOH2 (Example 2)	IOH4 (Example 4)	IOH5 (Example 5)	Melamine cyanurate
44	88.5			1.5				10
45	83.5			1.5				15
46	88.5					1.5		10
47	83.5					1.5		15
48		84.25			0.75			15
49			84.25		0.75			15
50	84.25						0.75	15

Table 4e **Formulations used in Examples 7 to 20**

Formulation	Nylon12	IOH2 (Example 2)	Melamine cyanurate	Calcium stearate	Zinc Stearate	Int38	Luwax EAS1	Irganox
51	83.25	0.75	15	1				
52	82.25	0.75	15	2				
53	83.25	0.75	15		1			
54	82.25	0.75	15		2			
55	82.25	0.75	15			2		
56	82.25	0.75	15				2	
57	83.75	0.75	15					0.5

Example 7: Processing rheology (Table 5), XRD & TEM
 (Figure 2), mechanical (Table 6) and fire
 performance (Tables 7 & 8) of nylon12
 modified with commercially available clay
 during melt processing.

The following example indicates that the processing
 rheology of Nylon 12 is not affected by the melt
 dispersion of commercially available 'organoclay' at least
 partially on a nanometer scale (XRD). This dispersion
 results in improved mechanical performance and heat
 release rate as determined by cone calorimetry but poor
 performance compared with conventional flame retarded
 nylon 12 (Nylon12 FR) in terms of vertical burn results
 which is a primary tool used to discriminate material fire
 performance by governing bodies such as UL, ASTM, FAA and
 the like. As such these materials do not meet such
 performance standards

20

Table 5 Torque Rheology

Extrusion Torque Rheology					
Formulation	Nylon12	1	2	3	4
Torque (Nm)	105	100	95	91	87
Batch mixer torque rheology					
Formulation	Nylon12	3	5	6	
Torque (Nm)	47	44	47	49	

Table 6 Mechanical Performance

Formulation	Nylon12	Nylon12 FR	1	2	3	4
Modulus (MPa)	1110	1712	1187	1227	1470	1700
Tensile Strength (MPa)	36	48	53	52.3	57	44.6
Impact (kJ/m ²)	4006	2200	6200	8100	6700	3700

Table 7 Fire Testing Cone Results

5

Formulation	Peak Heat Rel ^d kW/m ²	Mass Loss Rate g/m ² s	CO Prod ⁿ Kg/Kg	CO ₂ Prod ⁿ Kg/Kg	SEA (Smoke) m ² /Kg
Nylon 12 FR	1800	18.6	0.01	1.2	100
Nylon12	1344	17.1	0.03	1.6	385
1	740	13.3	0.01	1.0	360
2	620	12.8	0.02	1.5	382
3	536	10.8	0.02	1.5	382
4	447	10.0	0.02	1.5	410

Table 8 Vertical Burn Results

Formulation	UL94 (3.2 mm)	FAA (1.6 mm)
Nylon 12 FR	VO	Pass
Nylon12 LV	HB	Fail
1	V2	Fail
2	V2	Fail
3	V1	Fail
4	V1	Fail

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Example 8: Processing (Table 9), XRD (Figure 3),
mechanical (Table 10) and fire performance
(Table 11-14) of nylon12 modified with
commercially available clay and flame
5 retarding additives (melamine cyanurate)
during melt processing

The following example indicates that the processing
rheology of Nylon 12 is not effected by the melt
10 dispersion of commercially available 'organoclay' at least
partially on a nanometer scale (XRD) and flame retardant.
This dispersion results in improved mechanical performance
reduced heat release results via cone calorimetry and
vertical burn performance for specimens greater than 1.6
15 mm thickness compared with conventionally flame retarded
nylon12. Although samples of 0.75mm thickness provide good
smoke and toxic gas release results they fail FAA type 12
sec vertical burn testing and perform badly in radiant
panel tests. This indicates that the strategy is not
20 satisfactory to meet the performance of thin parts to the
performance requirements of governing bodies such as the
FAA.

Table 9 Processing Rheology

Formulation	Torque (Nm)
Nylon 12	105
7	102
8	104
9	107

Table 10 Mechanical Performance

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Notched Impact Strength (J/m ²)
Nylon12	1110	36	640	4600
Nylon12 FR	1712	48.1	77	2100
7	1505	38.5	54	3100
8	1471	38.1	222	4100
9	1380	38.1	291	4600

Standard Deviation -Modulus<4%, Strength<3%,
Elongation<10%, Impact <11%

5

Table 11 Fire Testing Cone Calorimetry

Formulation	Peak Heat Rel ^d kW/m ²	Mass Loss Rate g/m ² s	CO Prod ⁿ Kg/Kg	CO ₂ Prod ⁿ Kg/Kg	SEA (Smoke) m ² /Kg
Nylon 12 FR	1800	18.6	0.01	1.2	100
Nylon12	1344	17.1	0.03	1.6	385
7	670	13.9	0.01	1.6	220
8	695	14.1	0.01	1.6	240
9	782	16.1	0.01	1.7	280

Table 12 Vertical Burn Results

10

Formulation	UL94 (3.2 mm)	FAA 12s (1.6 mm)	FAA 12s (0.75 mm)
Nylon 12 FR	V0	Pass	Fail
Nylon12	HB	Fail	Fail
7	V0	Pass	Fail
8	V0	Pass	Fail
9	V0	Pass	Fail

Table 13 Vertical Burn, Radiant Panel and Smoke Test
Results (0.75mm)

Formulation	FAA 12s (0.75mm)	Smoke Ds	Radiant Panel
9	Fail	4.88	Full length burn
8	Fail	11.86	Full length burn
7	Fail	21.45	Full length burn

5

Table 14 Toxic Gas Emission

Toxic Gas (ppm)	Formulation		
	9	8	7
HF	3	3	5
HCl	1	1	3
HCN	4	4	4
H ₂ S	-	-	-
NO _x	2	2	1
HBr	1	1	1
PO ₄	-	-	-
SO ₂	1	1	1

Example 9: Processing rheology (Table 15), XRD (Figure 4), mechanical (Table 16) and fire performance (Table 17-19) of nylon12 modified with IOH2 incorporating montmorillonite modified with melamine hydrochloride/melamine and flame retarding additives (melamine cyanurate) during melt processing

10 *The following example indicates that the processing rheology of Nylon 12 is not effected by the melt dispersion of IOH2 and flame retardant at least partially on a nanometre scale (XRD). Such dispersion results in improved mechanical and vertical burn results compared*
15 *with conventionally flame retarded nylon12. Samples of 0.75 mm provide good smoke and toxic gas release results, pass FAA type 12s vertical burn tests and perform better in radiant panel tests. It is known to those in the art that flame retarding thin polymeric based materials is*
20 *much more difficult than flame retarding thicker materials and as such meeting performance requirements at thin thickness is an indication of superior fire retarding performance.*

25

Table 15 Processing Rheology

Formulation	Extruder Torque (Nm)
Nylon 12	105
11	105
12	106
13	103

Table 16 Mechanical Performance

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Notched Impact Strength (J/m ²)
Nylon12	1110	36	640	4600
Nylon12 FR	1712	48.1	77	2100
11	1443	39.7	140	3900
12	1398	39.0	215	4200
13	1349	38.9	375	4700

Standard Deviation -Modulus<3%, Strength<3%,
Elongation<8%, Impact <9%

5

Table 17 Fire Performance - Vertical Burn

Formulation	UL94 (3.2 mm)	12s FAA (1.6 mm)	12s FAA (0.75 mm)	60s FAA (0.75mm)
Nylon12 FR	VO	Pass	Fail	Fail
Nylon12	HB	Fail	Fail	Fail
11	VO	Pass	Pass	Pass
12	VO	Pass	Pass	Pass
13	VO	Pass	Pass	Pass

Table 18 Fire Performance (0.75mm)

Formulation	FAA 12s Vertical Burn Extinguishment time Burn length Drip Extinguishment time	Smoke Ds	Radiant Panel Extinguishment time & Burn length
11	4.9 s 46mm 0 s	6.79	5 sec 25 mm
12	2 s 19mm 0 s	9.83	3 sec 25mm
13	0 s 21 mm 0 s	3.31	1 sec 12.5 mm

Table 19 Toxic Gas Emission

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Toxic Gas Emission (ppm)	Formulation		
	13	12	11
HF	6	4	3
HCl	1	1	1
HCN	8	7	7
H ₂ S	-	-	-
NO _x	3	2	2
HBr	1	1	1
PO ₄	-	-	-
SO ₂	1	1	1

Example 10: The following example illustrates the effect of different processing parameters on the mechanical performance (Table 20) and vertical burn performance (Table 21) of formulation 13 which incorporates IOH2 + conventional flame retardant melamine cyanurate

Results indicate the robustness of the formulation in terms of mechanical and fire performance to different processing conditions such as through-put, temperature profile, screw speed for the given screw and barrel configuration provided in Figure 1.

Table 20 Mechanical Performance

Conditions			Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)
Processing Temp. (°C)	Screw speed (rpm)	Through-put (Kg/h)			
180	300	1.5	1300	37.6	5100
190	300	1.5	1420	37.9	5300
200	300	1.5	1420	38.4	4800
210	300	1.5	1520	38.8	4600
200	150	1.5	1500	37.7	5300
200	400	1.5	1530	39.6	4100
200	300	15	1540	39.4	4100

Standard Deviation -Modulus<3%, Strength<3%, Impact <9%

**Table 21 FAA 12s Vertical Burn Performance
(0.75mm thickness)**

Conditions			Result	Flame out Time (sec)
Processing Temp.(°C)	Screw speed (rpm)	Through-put (Kg/h)		
180	300	1.5	Pass	5
190	300	1.5	Pass	4
200	300	1.5	Pass	2
210	300	1.5	Pass	6
200	150	1.5	Pass	2
200	400	1.5	Pass	7
200	300	15	Pass	3

- 5 Example 11: The following example illustrates the effect
 of different IOH2 (Example 2) and melamine
 cyanurate concentrations on mechanical and
 vertical burn performance of nylon12 (Table
 22)

10

*Results indicate that preferably more than 10% melamine
 cyanurate is required to pass FAA 12 s vertical burn test
 requirements at 0.75 mm thickness. Results also indicate
 that unlike classically flame retarded nylon12 this fire
 performance is achievable whilst maintaining excellent
 mechanical properties relative to nylon12.*

15

Table 22 Performance of Formulations incorporating different concentrations of IOH2 and Melamine cyanurate

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)	FAA 12s Vertical burn (0.75mm) Ext. Time (s)
Nylon12	1100	36	4600	Fail (62)
Nylon12 FR	1712	48.1	2100	Fail (24)
11	1443	39.7	3900	Pass (5)
12	1398	39.0	4200	Pass (5)
13	1349	38.9	4700	Pass (2)
14	1480	37.9	4200	Pass (14)
15	1410	39.4	4400	Pass (7)
16	1386	40.1	4800	Pass (6)
17	1483	37.9	3900	Fail (18)
18	1476	39.4	5050	Fail (19)
19	1404	40.1	5200	Fail (19)
20	1445	37.8	4200	Fail (32)
21	1420	39.7	4500	Fail (28)
22	1361	40.1	5200	Fail (32)

5 Example 12: The following example illustrates the effect of different conventional flame retardants on the performance (Table 23) of nylon12 incorporating an IOH2 (Example 2)

10 *The results presented in Table 23 demonstrate that materials incorporating the IOH and melamine cyanurate provide both excellent mechanical and fire performance. Formulations containing melamine phthalate and pentaerythritol phosphate also provide excellent fire*

15 *performance with lower mechanical performance. Samples containing IOH with melamine cyanurate and Mg(OH)₂ provide the excellent mechanical performance in terms of impact, modulus, and strength also excellent vertical burn performance.*

**Table 23 Performance of formulations incorporation IOH2
and various conventional flame retardants**

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)	FAA 12 s vertical burn (0.75mm) Ext. Time (sec)	UL 94 3.2 mm
12	1460	39	4800	Pass (2)	V0
23	1500	41	3900	Fail (31)	V2
24	1540	41.9	2500	Fail (26)	V2
25	1500	40.4	3000	Fail (29)	V2
26	-	-	-	Pass (7)	V0
27	1410	41.0	4100	Fail (24)	V2
28	1420	43.5	1500	Fail (32)	V2
29	1160	43.6	800	Pass (10)	V0
30	1628	43.6	4800	Pass (4)	V0

5

Example 13: The following example illustrates the effect of removing components of the fire resistant formulation on resultant fire performance (Table 24)

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The results indicate that removal of either the modified inorganic-organic hybrid or melamine cyanurate from the formulation provides unsatisfactory vertical burn performance following FAA 12 s type testing at 0.75mm thickness.

15

Table 24 FAA type Vertical Burn Performance (0.75mm)

Formulation	Ext. Time (s)	FAA requirement
Nylon12	65 ± 9	Fail
31	31 ± 4	Fail
32	32 ± 13	Fail
15	7 ± 4	Pass

- Example 14: The following example illustrates the
mechanical and 12s vertical burn
performance (Table 25) and cone calorimetry
results (Table 26) of Nylon12 formulations
prepared with IOH2 (Example 2), melamine
cyanurate and magnesium hydroxide. Table
27 provides radiant panel, smoke, and 60s
FAA type vertical burn results for the
above mentioned formulations. Mechanical
and vertical burn performance of Nylon12
formulations incorporating IOH2, melamine
cyanurate and magnesium hydroxide of
different surface functionality and
particle size distribution is provided in
Table 28.
- Results from Example 14 show that excellent processability, mechanical, vertical burn, and heat release results are obtainable with formulations incorporating IOH2, melamine cyanurate and low concentrations of magnesium hydroxide in particular formulations incorporating IOH dispersed at least partially on a nanometre scale, melamine cyanurate and 2.5% magnesium hydroxide which provides excellent mechanical, vertical burn and peak and average heat release results. The results also indicate that Mg(OH₂) of different grades may be employed in conjunction with IOH2 and melamine cyanurate to produce formulations with excellent processability, mechanical and fire performance.

Table 25 Mechanical Performance of nylon materials with various amounts of IOH2 and conventional flame retardants

Formulation	MFI (g/min)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)	FAA 12s Vertical burn Ext. Time (s) (0.75mm)
Nylon12	44	1100	36	4600	Fail (62)
Nylon12 FR	32	1712	48.1	2100	Fail (24)
33	12.6	1470	41.8	4500	Fail (18)
34	12.0	1460	41.1	4700	Pass (10)
35	11.5	1430	39.9	5200	Pass (9)
36	13.4	1578	43	3800	Pass (6)
30	13.5	1509	42	4800	Pass (4)
37	13.5	1543	40.5	5300	Pass (6)
38	13.4	1529	41	3900	Fail (41)
39	13	1520	40.6	4200	Fail (19)
40	13.1	1510	41.6	4600	Pass (4)

5

Table 26 Cone Calorimeter Heat Release Results

Formulation	Peak Heat Release (kW/m ²)	300s Average Heat Release (kW/m ²)
Nylon12	1100	748
Nylon12 FR	1712	640
18	1314	707
21	1643	680
12	1595	676
39	1147	552
30	1001	578
34	885	491

Table 27 Comparison of fire performance of various formulations containing IOH2 dispersed at least partially on a nanometre scale, melamine cyanurate and optionally magnesium hydroxide H7

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Formulation	Radiant Panel Extinguishment time & Burn length (average)	Smoke Ds	Toxic Gas (FAA requirement)	FAA 60 Second Vertical burn (0.75mm) (Extinguishment time seconds)
Nylon12	-	21	Pass	-
22	-	11.7	Pass	-
21	-	10.4	Pass	-
20	-	7.8	Pass	-
19	-	11.3	Pass	-
18	-	11.4	Pass	Fail (20)
17	-	8.1	Pass	Pass (9)
13	1 second 12.4 mm	14.5	Pass	Pass (0)
12	-	14.4	Pass	Pass (0)
11	-	7.5	Pass	Fail (133)
39	-	15	Pass	Fail (58)
30	-	14.5	Pass	Pass (15)
34	2.5 second 15.0 mm	11.3	Pass	Pass (7)

Table 28 Performance of materials incorporating IOH2 melamine cyanurate and Mg(OH)₂ with various particle size and surface functionality

Formulation	MFI (g/min)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)	FAA 12s Vertical burn Ext. Time (s) (0.75mm)
34	13.5	1480	40.4	5100	Pass (6)
41	11.5	1420	41	5000	Pass (6)
42	16.2	1470	40.2	5300	Pass (13)
44	12.4	1470	40.4	5300	Pass (14)

5

Example 15: The following example illustrates the mechanical and vertical burn performance (Table 29) of Nylon12 formulations prepared with the inorganic-organic hybrids outlined in Examples 1, 2 & 4 and melamine cyanurate

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The results indicate superior fire performance of nylon12 formulations containing the intercalated and modified IOH (Examples 2 and 4) compared with that prepared with just melamine hydrochloride modified IOH (Example 1).

15

Table 29 Mechanical and Vertical Burn Performance

Formulation	Tensile Strength (MPa)	Tensile Modulus (MPa)	Notched Impact Strength J/m ²	0.75 mm FAA 12 sec Vertical Burn (Ext. time sec)
44	41.7	1490	5000	Fail (22)
45	39.5	1531	4100	Pass (12)
46	40.1	1580	4600	Pass (2)
47	39.2	1550	4100	Pass (5)
18	40.4	1590	4700	Fail (19)
12	39.3	1628	4000	Pass (3)

Standard Deviation -Modulus<5%, Strength<5%, Impact <10%

Example 16: The following example illustrates the performance of nylon6 and nylon66 formulations incorporating IOH2 and melamine cyanurate

The results indicate that IOH2 at least partially dispersed on a nanometre scale in conjunction with melamine cyanurate provides excellent mechanical and vertical burn performance relative to nylon6 and nylon66.

Table 30 Mechanical and Vertical Burn Performance

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)	FAA 12s Vertical burn Ext. Time (s) (0.75mm)
Nylon6	2720	76	1900	Fail (61)
48	2970	73.5	2000	Pass (1)
Nylon66	2890	83.5	1900	Fail (65)
49	3500	67	1900	Pass (1)

Example 17: The following example shows the XRD of nylon 12 formulations incorporating modified and intercalated hectorite (Example 6) dispersed at least partially on a nanometre scale (Figure 5) and melamine cyanurate and the formulations vertical burn performance (Table 31)

The XRD results indicate that hectorite is modified owing to its larger intergallery spacing compared with the starting material. Nylon12 incorporating IOH5 at least partially dispersed on a nanometre scale (Figure 5) and melamine cyanurate show excellent fire performance.

Table 31 Vertical Burn Performance

Formulation	FAA 12s Vertical burn, Ext. Time (s)(0.75mm)
Nylon12	Fail (68)
50	Pass (2)

- 5 Example 18: This example shows the rheology (Table 32)
and mechanical and vertical burn
performance (Table 33) of formulations
incorporating IOH2, conventional flame
retardant and minor processing additives.
- 10 *This example illustrates that reductions in viscosity*
across a range of shear rates of the formulations
incorporating nylon12, IOH2 and conventional flame
retardants through the addition of (additional) minor
processing additives during processing. This reduction in
15 *viscosity is possible with out a significant reduction in*
mechanical performance and generally without compromising
fire performance particularly under the stringent
conditions required to fire retard thin materials to meet
performance standards outlined by various regulatory
20 *bodies.*

Table 32 Rheology of formulations at different shear rates and corresponding MFI data

Formulation	Shear rate				MFI
	10 ⁻²	10 ⁻¹	10 ⁰	10 ¹	
	Viscosity (Pas)				g/min
Nylon12	223	169	106	108	35
13	13100	1750	300	124	29
34	719	624	560	502	13
51	4800	1040	226	128	34
52	1920	6590	1560	95	39
53	1100	865	168	95	39
54	554	865	162	95	41
55	98300	1930	335	143	33
56	13500	1870	284	106	31

5

Table 33 Mechanical and Vertical Burn Performance

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength (J/m ²)	0.75 mm FAA 12 sec Vertical Burn (Extinguishment time (s))
Nylon12	1100	36	4600	Fail (62)
13	1349	38.9	4700	Pass (2)
34	1480	40.4	5100	Pass (6)
51	1215	35.8	3500	Pass (3)
52	1165	35.5	3500	Pass (2)
53	1233	36.4	3500	Pass (13)
54	1176	35.3	3300	Fail (25)
55	1168	33.3	3300	Pass (8)
56	1241	35	3700	Pass (10)

Example 19: This example provides the mechanical and fire performance (Table 34) of nylon12 formulations incorporating IOH2, conventional flame retardants and minor component of stabilizer.

The results indicate that the mechanical and vertical burn performance of formulations containing nylon12, IOH2 conventional flame retardant is not significantly reduced by addition of additional stabilizer to the formulation during compounding.

Table 34 Mechanical and Vertical Burn Performance

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Notched Impact Strength J/m ²	0.75 mm FAA 12 sec Vertical Burn (Extinguishment time (s))
Nylon12	1100	36	4600	Fail (62)
13	1349	38.9	4700	Pass (2)
57	1394	39.1	4800	Pass (4)

Example 20: This example shows that formulations incorporating IOH's may not only be fabricated into materials, components and parts of components by processes such as extrusion, injection moulding, compression moulding and alike but also by low shear processes such as rotational moulding (Figure 6) and selective laser sintering.

Figure 6 provides examples of components manufactured by rotational moulding employing formulations incorporating IOH2, melamine cyanurate optionally magnesium hydroxide and other additives such as but not limited to formulation 13 and 34. The examples illustrate that such formulations show suitable thermal / oxidative stability and melt

- 60 -

rheology for manufacturing components under low shear and thermally demanding environments.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.